

PATENT ABSTRACTS OF JAPAN

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(54) LITHIUM SECONDARY BATTERY**(57)Abstract:**

PURPOSE: To provide a lithium secondary battery which has high energy density and superior in charge/discharge cycle characteristics.

CONSTITUTION: A lithium secondary battery is provided with a positive electrode which uses a metal compound (metal compound oxide, metal chalcogenide, etc.,) possible of implantation and emission of lithium ion as an active material and a negative electrode which uses nonaqueous electrolytic solution, and carbon material or lithium metal possible of implantation and emission of lithium ion, as active materials, and the nonaqueous electrolytic solution contains hydroquinone or hydroquinone derivatives.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to a lithium secondary battery useful as a power supply for a drive of sized electronic equipment.

[0002]

[Description of the Prior Art]In recent years, research of the lithium secondary battery is briskly advanced as a high-energy-density type rechargeable battery. Generally And LiCoO_2 which these lithium secondary batteries can emit [insertion and], [of a lithium ion] The anode which uses metal chalcogen ghosts, such as metal multiple oxides, such as LiNiO_2 , MoS_2 , V_6O_{13} , as an active material, It comprises a negative electrode which uses as an active material the carbon material and lithium metal of a lithium ion in which insertion and discharge are possible, and an electrolysis solution which dissolved lithium salt, such as LiPF_6 and LiClO_4 , in nonaqueous solvents, such as propylene carbonate, 1, and 2-dimethoxyethane, as electrolytes.

[0003]

[Problem(s) to be Solved by the Invention]Generally, as for the efficiency of the charge and discharge of a lithium secondary battery, the reversibility in the cell reaction of positive active material and negative electrode active material, the stability of the electrolysis solution itself, and the reaction stability of an electrolysis solution and an active material influence greatly.

[0004]By the way, since the electromotive force of a lithium secondary battery was as high as 4V, the decomposition reaction of the electrolysis solution arose, quantity of electricity was consumed, and it had the problem that the efficiency of charge and discharge fell.When a resultant with high electrical resistance covers an electrode by change of the electrolysis solution presentation by disassembly of this electrolysis solution, or disassembly of the electrolysis solution which occurs on the surface of an anode or a negative electrode, Since the internal resistance of a cell increased and charge and discharge became difficult, when charge and discharge were repeated, it had the problem that cell capacity fell remarkably.

[0005]Then, the purpose of this invention solves the above-mentioned problem, has a high energy density, and there is in providing the lithium secondary battery excellent in the charge-discharge cycle characteristic.

[0006]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, a lithium secondary

battery of this invention, Consisting of an anode which uses as an active material metallic compounds in which insertion and discharge of a lithium ion are possible, nonaqueous electrolyte, and a negative electrode which uses as an active material a carbon material or a lithium metal of a lithium ion in which insertion and discharge are possible, said nonaqueous electrolyte contains hydroquinone or a hydroquinone derivative.

[0007]And a hydroquinone derivative is characterized by being what is expressed with the following formula (however, R CH₃ or C₂H₅).

[0008]

[Formula 2]

ID=000003

[0009]hydroquinone or a hydroquinone derivative -- the inside of nonaqueous electrolyte -- 0.1 - 1.0wt% -- it contains

[0010]The solvent in nonaqueous electrolyte At least one sort in propylene carbonate and ethylene carbonate, At least one sort in 1,2-dimethoxyethane, 1,2-diethoxyethane, and dimethoxy carbonate to what was mixed at a rate of 90-30:10-70 by the volume ratio. hydroquinone or a hydroquinone derivative -- 0.1 - 1.0wt% -- it is added

[0011]As nonaqueous electrolyte in this invention, among high dielectric constant solvents, such as propylene carbonate and ethylene carbonate, namely, any one sort, Among lower dielectric constant solvents, such as 1,2-dimethoxyethane, 1,2-diethoxyethane, and dimethyl carbonate, any one sort, In the solvent which was respectively mixed in 90-30:10-70 by the volume ratio, and added any one sort of hydroquinone or the hydroquinone derivative further, What dissolved lithium salt, such as LiPF₆,

LiClO₄, LiBF₄, and LiAsF₆, as an electrolyte can be used. In this case, although electrolytic concentration in particular is not limited, its 0.1 or more mol/L is preferred.

[0012]As positive active material, LiCoO₂, LiNiO₂, What is necessary is just a substance in which insertion and discharge of lithium ions, such as metal chalcogen compounds, such as metal multiple oxides, such as LiMn₂O₄, or MoS₂, V₆O₁₃, and Mo₆S₈, are possible.

[0013]As negative electrode active material, things are possible using a carbon material in which insertion and discharge of a lithium ion are possible, or metal lithium.

[0014]The separator can use porosity polypropylene film production, a nonwoven fabric made from porosity polypropylene, a nonwoven fabric made from glass fiber, etc.

[0015]In addition, a general thing more publicly known than before can be suitably used for battery construction parts, such as a charge collector, a gasket, an obturation board, and a positive electrode can.

[0016]

[Function]The lithium secondary battery of this invention contains hydroquinone or a hydroquinone derivative in nonaqueous electrolyte. This hydroquinone or a hydroquinone derivative reacts to the activity radical generated from a solvent or an electrolyte at the time of disassembly of an electrolysis solution like a lower type. Pin formula * shows an activity radical.

[0017]

[Formula 3]

ID=000004

[0018]A tunic with high electrical resistance can be prevented from an activity radical being consumed and being generated by this reaction on the surface of an electrode. As a result, even if it repeats charge and discharge, the fall of the cell capacity by internal resistance rise of a cell is suppressed.

[0019]Although the mechanism cannot be solved, the initial capacity of a cell also becomes large by adding hydroquinone or a hydroquinone derivative.

[0020]

[Example]Hereafter, the example is described about the lithium secondary battery of this invention.

Drawing 1 is a sectional view of the coin type cell obtained by one example of this invention. In the figure, the charge collector in which, as for 1, a negative electrode, the separator of the product [2 / 3 / an anode and] made from polypropylene, and 4 consist of aluminum plates, the positive electrode can into which 5 processed the stainless steel plate, the obturation board into which 6 similarly processed the stainless steel plate, and 7 are insulating gaskets.

[0021]Next, the manufacturing method of the lithium secondary battery of this invention is explained. First, the negative electrode 1 was produced. That is, after calcinating in reducing atmosphere with a temperature of 1800-2500 **, using petroleum coke as a starting material, it ground and the negative electrode active material of the carbon material was obtained. 10wt% of the fluoro-resin system binder was added into material in this end of carbon powder, N-methyl-pyrrolidone solution was made suspended and these were made into the slurry. Then, on the aluminum plate 4 prepared as a charge collector, it molded into the sheet shaped by the doctor blade method, and the negative electrode 1 was obtained.

[0022]Next, the anode 2 was produced. That is, cobalt carbonate was mixed with lithium carbonate, to the cobalt-acid-lithium (LiCoO_2) powder which was calcinated for 20 hours and compounded at 1000

**, a proper quantity of fluoro-resin system binders were mixed with the carbon powder which is a conducting agent, application-of-pressure molding was carried out, and the laminated anode 2 was produced.

[0023]Next, the electrolysis solution of the presentation shown in Table 1 was produced. In this case, ethylene carbonate or propylene carbonate is used as a high dielectric constant solvent, LiClO_4 or LiPF_6 was used as an electrolyte, using hydroquinone, hydroquinone monomethyl ether, or hydroquinone monoethyl ether as an additive agent, using dimethoxyethane or dimethyl carbonate as a lower dielectric constant solvent. In Table 1, it is a thing besides the range of this invention which attached * seal.

[0024]

[Table 1]

ID=000005

[0025] Then, as shown in drawing 1, as the above-mentioned negative electrode 1 and the above-mentioned anode 2 were inserted via the separator 3 made from polypropylene with the charge collector 4 which consists of an aluminum plate of a couple, they were accommodated in the positive electrode can 5. And the separator 3 was impregnated with the above-mentioned electrolysis solution. Then, it was obturated with the obturation board 6 in the state where the circumference was insulated with the positive electrode can 5 by the insulating gasket 7, and 14 sorts of lithium secondary batteries with which electrolysis solutions differ were produced.

[0026] About the lithium secondary battery obtained above, while checking initial capacity as service capacity from 4.2V to 2.0V by current density 0.5 mA/cm², The cell capacity after doing 100 charge and discharge tests similarly under the conditions of charge and discharge current density 0.5 mA/cm², the charge final voltage 4.2V, and the discharge final voltage 2.0V was checked. These results are shown in Table 2.

[0027]

[Table 2]

ID=000006

[0028]As for the sample numbers 1, 3, 5, and 7 which are within the limits of this invention which uses the electrolysis solution which added hydroquinone or a hydroquinone derivative, in early cell capacity, the cell capacity after 245 or more Ah/kg and 100 cycles indicates the large value to be 220 or more Ah/kg as shown in Table 2.

[0029]However, like the sample number 9, when the addition of hydroquinone or a hydroquinone derivative exceeds 1.0wt%, early cell capacity has the cell capacity as small as 170 Ah/kg after 200 Ah/kg and 100 cycles, and is not preferred. On the other hand, as shown in the sample numbers 2, 4, 6, 8, 10, 12, and 14, when the addition of hydroquinone or a hydroquinone derivative is 0, early cell capacity has the cell capacity as small as 175 or less Ah/kg after 235 or less Ah/kg and 100 cycles, and is not preferred.

[0030]As shown in the sample number 11, when a lower dielectric constant solvent exceeds 70vol% less than [30vol%] in a high dielectric constant solvent, early cell capacity has the cell capacity as small as 160 Ah/kg after 195 Ah/kg and 100 cycles, and is not preferred. On the other hand, as shown in the sample number 13, when a lower dielectric constant solvent is not included only with a high dielectric constant solvent, early cell capacity has the cell capacity as small as 170 Ah/kg after 210 Ah/kg and 100 cycles, and is not preferred.

[0031]In the above-mentioned example, the mixture of a poly alkyl system binder or a fluoro-resin system binder, and a poly alkyl system binder, etc. can be used as a negative electrode or a binder for anode formation in addition to a fluoro-resin system binder.

[0032]A press-forming method, roll diffusion bonding, etc. of a mixture which consist of a doctor blade method, a spin coat method, an active material, a binder, etc. of the slurry which consists of an active material, a binder, a solvent, etc. as a formation method of a negative electrode or an anode are employable suitably.

[0033]It is possible for it not to be limited to aluminum but to use suitably metallic materials, such as copper, aluminum, iron, and stainless steel, as construction material of the charge collector 4.

[0034]

[Effect of the Invention]By the above explanation, the lithium secondary battery of this invention contains hydroquinone or a hydroquinone derivative in nonaqueous electrolyte so that clearly. With this hydroquinone or a hydroquinone derivative, it has a high energy density and the lithium secondary battery excellent in the cycle characteristic can be obtained.

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CLAIMS

[Claim(s)]

[Claim 1]A lithium secondary battery comprising:

An anode which uses as an active material metallic compounds in which insertion and discharge of a lithium ion are possible.

Nonaqueous electrolyte.

Consisting of a negative electrode which uses as an active material a carbon material or a lithium metal of a lithium ion in which insertion and discharge are possible, said nonaqueous electrolyte is hydroquinone or a hydroquinone derivative.

[Claim 2]The lithium secondary battery according to claim 1, wherein a hydroquinone derivative is what is expressed with the following formula (however, R CH_3 or C_2H_5).

[Formula 1]

ID=000002

[Claim 3]hydroquinone or a hydroquinone derivative -- the inside of nonaqueous electrolyte -- 0.1 - 1.0wt% -- the containing lithium secondary battery according to claim 1 or 2.

[Claim 4]A solvent in nonaqueous electrolyte At least one sort in propylene carbonate and ethylene carbonate, At least one sort in 1,2-dimethoxyethane, 1,2-diethoxyethane, and dimethoxy carbonate to what was mixed at a rate of 90-30:10-70 by a volume ratio. hydroquinone or a hydroquinone derivative -- 0.1 - 1.0wt% -- the lithium secondary battery according to claim 1 or 2 adding.

[Translation done.]